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Measurement of Naturally Occurring Radioactive Materials (NORM) in produced water, in some Iranian oil fields using gamma spectroscopy

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Abstract.

In this research, the concentration of natural radioactive materials (NORM) in produced water was measured using gamma spectroscopy method by HPGe detector. Samples from desalination plants were prepared in accordance with the principles of sampling. Measurements on collected samples were performed to evaluate Ra-226, Th-232 and K-40 concentrations. Specific activity of Ra-226, Th-232 and K-40 were in the range of 7.92±0.74 to 68.12±0.087 Bq/L, from background level to 30.73±2.9 Bq/L and from background level to 34.65±1.36 respectively. Ra-226 activity in all the stations was above Derived Release Limit of Canada and EPA standard. According to the results, Environmental effects must be taken into consideration when releasing the produced water..

Keywords: Natural radioactivity; produced water; spectroscopy; gamma ray; HPGe detector; oil fields; Iran.

1. Introduction

Naturally Occuring Radioactive Materials (NORM) are substances that are found naturally in the environment. These materials are found in water, soil, plants, human body, coal, ore, geothermal waste disposal, waste water and etc. In low but variable quantities [1]. NORMs exist in the earth's crust and can be concentrated and expanded by oil and gas reprocessing operations [2]. These materials are usually related to the decay chains of U-238, Th-232 and their daughter nuclei. The average concentration of uranium and thorium in the earth's crust were measured 4.2 and 12.5 ppm respectively [1]. With the expansion of industrial activities, the cincentration of these materials also increase. These materials are dispersed as result of human activities or some industrial processes. Industrial deposits, drilling mud and layers adhering to the tubes are examples of substances that have high levels of natural radioactivity and may be moved from place to place and reused [3]. Uncontrolled activities can pollute the environment and endanger the health of organisms. Measurements carried out on various oil and gas fields show that there is not significant amount of U-238 and Th-232 in oil and gas

production facilities. The chemical solubility of these elements is low, non-movable and can not move from the reservoir. The water produced in the extraction process contains cations of groupe 2 of periodic table. Calcium, Strontium, Barium and Radium are dissolved from the reservoir rock into the produced water and transported outside. Thus the produced water contains isotopes of Ra-226 from the chain of U-238, Ra-228 and Ra-224 from Th-232 chain [3]. All three three isotopes- not their parents- are present in produces water with oil and gas. When ions in the groupe 2 elements, which include Radium, are detected in the produced water, the pressure and temperature drop will reduce the solubility of their sulfates and carbonates which preciptate in operation facilities,pumps,seperators, storage tanks, valves and etc. The NORM pollution of oil and gas facilities is usual and extensive. Some contaminants may be severe enough to expose workers with haardous concentrations. Discharged produced water from oil and gas activities in addition to hydrocarbons and suspended solids, they contain saline, heavy metals, radioactive materials, soluble organic substances, and any other chemical materials that is added during the process of seperating oil from water. Removal of surface water in nature can cause the introduction of these radioactive substances into the environment and ground water. Various measurements have been taken on natural radiation in produced water in egypt [4], syria [5] and kuwait. In 2009 Moattar and et al. Conducted a research on NORM in oil produced water from persian gulf fields and reported concentrations higher than the permitted limit [6]. NORM measurements is important from radiation protection point of view. Considering the statistical and no thresholds effects of radiation, the need for environmental measurements to protect the environment and workers against radiation is necessary. As the produced water enters evaporation ponds after seperation from oil in desalination complexes, it is likely to enter the ground water. On the other hand, awareness of radiation values will help for protecting workers against radiation. Therefore, there is a need for sufficient information on the level of radiation and emmition dose in oil regions.

2. Methods

2.1 sampling

sampling sites were desalination complexes of Karoon, Maroon, Aghajari and Ghachsaran oil producing companies. Sampling was carried out in accordance with the methodology provided by International Atomic energy Agency [7]. Before sampling, the reservoir water was drained for 2 minutes. 1.5 liters polyethylene containers were used that were washed by distilled water and acid in advanced. Before collecting the original sample was filled and emptied twice to prevent the adhesion of radioactive material to the container wall, 3 ml of hydrochloric acid (HCl) 11 M was added to the samples on site then the samples were transfered to 800 cm3 marinelli containers and sealed for 30 days to achieve radiactive equliberium between radium and it’s daughters. Desalination complexes were ahwaz 1, Ahwaz 2, ahwaz 4, Maroon 1, Maroon 3, Maroon 4, Rag sefid 1, Karanj Parsi, Gachsaran 2.

2.2 Introducing the detection system

the specific activity of nuclei in the decay chains of U-238, Th-232 and K-40 single isotope were performed by using a coaxial HpGe (ORTEC 10180 GMX0 and a multichannel analyer (MCA) with 4096 channels that was constructed by Iranian Institute of Applied

Physics (IAP). The Maestro software was used to analyze the spectrum. The energy resolution of detection system in 1332.15 Kev energy for Co-60 was calculated to be 1.3 Kev. The detection system had a shield consisting of 5 cm lead, 2 mm iron and 2 mm copper for removing background radiation. Energy callibration was done using Co-60, Cs-137 and Am-241 point sources and then for efficiency callibration of detector liquid reference sample in the same geometry of the unknown samples were used.

TABLE I. *PROPERTIES OF LIQUID REFERENCE SAMPLE AND CALCULATED EFFICIENCY*

Radioisotope	***Radioactivity (μCi)***	***Gamma energy (KeV)***	***Emission probability (%)***	***Efficiency (%)***
^{152}Eu	0.081±0.0007	121.78	28.58	2.2913
^{152}Eu	0.081±0.0007	244.69	7.58	1.3881
^{152}Eu	0.081±0.0007	344.27	26.5	1.0115
^{152}Eu	0.081±0.0007	411.234	2.234	0.7966
^{152}Eu	0.081±0.0007	778.9	12.94	0.4439
^{152}Eu	0.081±0.0007	864.37	4.245	0.3874
^{152}Eu	0.081±0.0007	964.07	14.6	0.3367
^{152}Eu	0.081±0.0007	1112.069	13.64	0.3074
^{152}Eu	0.081±0.0007	1408	21	0.2404

2.3 Gamma spectrum analysis method

After energy and efficiency calibration of detection system, unknown samples were placed on the detector in coaxial direction and counted for 86400 seconds. To correct the pure surface under full-energy peak background radiation was measured using a void sample (double-distilled water) in 800 cm3 marinelly container. Specific radioactivity was calculated using folliwing equation:

$$\mathrm{Act(Bq/L)} = \frac{C_{net}}{\varepsilon(\%)\times\lambda\times t\times V}\times 100 \qquad (1)$$

Where C_{net} is pure counting under the peak, ε is full-energy peak efficiency in desired energy and λ is gamma emission probability, t is the live counting time and V is sample volume. Pb-214 was used to To measure the concentration of Ra-226, Ac-228 was used to measure concentration of Th-232 which are in radiactive equilibrium of their mother nuclei. Used gamma lines for measurement and emission probabilities for each nucleus are shows in table 2.

TABLE II. GAMMA LINES USED FOR ACTIVITY MEASURMENTS

Radioisotope	***Gamma energy (KeV)***	***Emission probability (%)***	***Efficiency (%)***

^{40}K	1460.83	10.68	0.560
^{214}Pb	295.220	18.70	2.140
	351.930	35.80	1.960
^{214}Bi	609.320	45.00	0.890
	1120.28	14.90	1.340
^{228}Ac	338.400	11.51	20.07
	968.900	16.74	9.980

2.4 Calculation of the absorbed dose rate and effective dose rate.

Absorbed dose rate (D) of naturally occuring nuclei (K-40, Ra-226, Th-232) have been calculated considering uniform distribution of radioactive nuclei [8]. In this calculation , the effect of other natural radioactive nuclei have been neglected. Thus, according to UNSCEAR 2000 report, absorbed dose rate (D) will be equal to [9]:

$$D(\mu Gy/h) = 0.462 \times C_{Ra} + 0.621 \times C_{Th} + 0.0417 \times C_K \qquad (2)$$

Where C-Ra, C-Th and C-k are specific radioactivity of Ra-226, Th-232 and K-40 respectively and their coefficients are used to convert the radiation to the absorbed dose rate in air per unit volume. Effective dose rate per year (mSv/yr) is calculated using the following equation [9]:

$$D_{eff}(mSv/yr) = D \times 1.21 \times 10^{-3} \qquad (3)$$

External hazard index can be used to limit external radiation dose to the value of 1 mSv/yr [9]:

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \qquad (4)$$

In this equation, it is aasumed that 370 Bq/kg of Ra-226, 250 Bq/kg of Th-232 and 4810 Bq/kg of K-40 generate equal gamma dose rate. External hazard index should always be less then 1 so that the risk of radiation can be ignored [10].

2.5 Test of solved salts (TSS) on wastewater samples

Produced water samples contain large amounts of soluble salts in water. To achieve a criterion of impurity and hardness of samples, TSS was performed on produced water samples. The results of this test are presented in table 3.

TABLE III. TTS RESULTS

Sample name	*Place of sampling*	*Amount od dissilved saline (mg/L)*
W1	Ahwaz 2 desalination plant	48914
W2	Ahwaz 4 desalination plant	207881
W3	Ahwaz 1 desalination plant	184001
W4	Ahwaz 1 desalination plant	183268
W5	Maroon 1 desalination plant	238025
W6	Maroon 3 desalination plant	224097
W7	Maroon 4 desalination plant	188399
W8	Rag sefid 1 desalination plant	57757
W9	Keranj Parsi desalination plant	94451
W10	Gachsaran 2 desalination plant	105157

3. Results

In this research, the concentration of NORM in 10 produced water samples from the desalination complexes of south oil-rich regions was measured. Specific radioactivity of Ra-226, Th-232 and K-40 are shown in table 4. Radioactivity fluctuation for Ra-226, Th-232 and K-40 nuclei varies from 7.92±0.74 to 68.12±0.087, from background to 30.73±2.9 and from background to 27.57±1.37 Bq/L respectively. As the produced water enters the environment in some areas and in persian gulf operation stations there is probablity to to enter the sea, results can be compared to measurments which have done on the water samples from different parts of the world. Concentration of (NORM) in water as reported by researchers from different countries, are presented in table 5. According to table 5, radioactivity of Ra-226, Th-232 in produced water is more than environmentsl water radioactivity of Nigeria, Egypt, Braile, Saudi Arabia, Serbia, Japan, Turkey, Pakistan and Iran (Oman sea) and K-40 radioactivity is more than environmental water radioactivity of Egypt, Malaysia, Turkey and Pakistan and it is lower than Nigeria and Islamic Republic of Iran (Oman Sea). Dose rate (D), effective dose and H-ex for produced water samples are given in table 6. The dose rate varies from 5.71 to 51.94 nGy/h, with an average of 23.65 nGy/h, which is within the range provided in the UNSCEAR 2000 report. Effective dose varies from 6.91 to 62.84 μSv/yr and its average is 28.62 μSv/yr (0.02 mSv/yr). While the global average is approximately 0.5 mSv/yr. The external haard index varies from 0.03 to 0.3, with an average of 0.14, which is dramaticaly below the unit value.

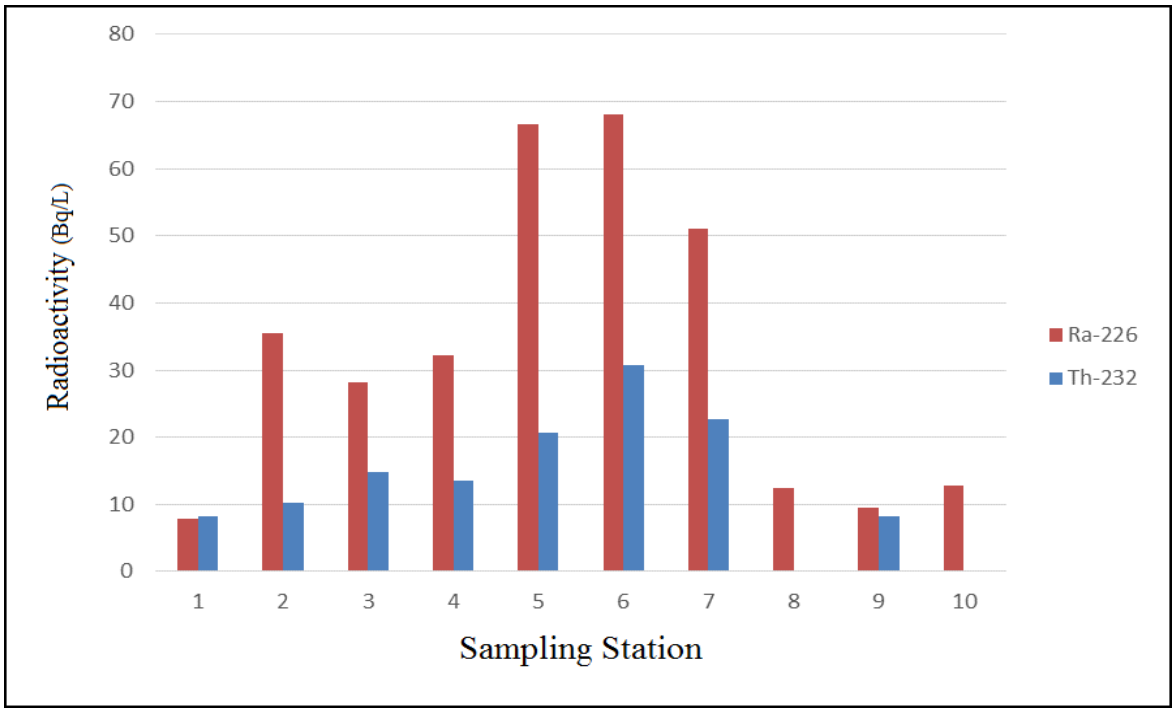

Fig. 1. Radioactivity concentration of ^{226}Ra, ^{232}Th in produced water samples

TABLE IV. SPECIFIC RADIOACTIVITY OF RADIOISOTOPES IN 10 SAMPLES

Sample name	***Place of sampling***	***Oil field***	***^{226}Ra (Bq/L)***	***^{232}Th(Bq/L)***	***^{40}K(Bq/L)***
W1	Ahwaz 2 desalination plant	Asmari & Bangestan	7.92±0.74	8.19±2.43	B. G.
W2	Ahwaz 4 desalination plant	Asamari	35.52±0.912	10.24±1.37	33.23±1.45
W3	Ahwaz 1 desalination plant	Asmari	28.22±0.65	14.78±1.94	B. G.
W4	Ahwaz 1 desalination plant	Bangestan	32.28±0.78	13.48±2.22	34.65±1.36
W5	Maroon 1 desalination plant	Maroon	66.6±0.81	20.69±2.14	28.48±1.48
W6	Maroon 3 desalination plant	Maroon	68.12±0.087	30.73±2.9	33.23±1.31
W7	Maroon 4 desalination plant	Maroon	50.99±0.82	22.74±2.02	27.57±1.13
W8	Rag sefid 1 desalination plant	Aghajari	12.37±0.65	B. G	B. G.
W9	Keranj Parsi desalination plant	Aghajari	9.51±0.46	8.19±1.99	B. G.

W10	Gachsaran 2 desalination plant	Gachsaran	12.81±0.59	B. G.	B. G.

TABLE V. ACTIVITY COMPARISION OF WATER SAMPLES IN DIFFERENT PARTS OF WORLD

Country	*Sample type*	*^{226}Ra (Bq/L)*	*^{232}Th(Bq/L)*	*^{40}K(Bq/L)*	*reference*
Nigeria	Lake water	8.4-20	8-21	7-130	[8]
Egypt	Lake water	0.021	0.006	0.119	[11]
Brazil	Underground water	0.01-3.79	-	-	[12]
Saudi Arabia	Well water	1.28-3.61	-	-	[13]
Serbia	Drinking water	0.26	-	-	[14]
Japan	Sea water	0.0014-0.0048	-	-	[15]
Malaysia		0.0266	0.0645	1.2	[16]
Turkey	Tank	0.003-0.045	-	0.009-0.29	[17]
Pakistan	Drinking water	0.011	0.005	0.14	[18]
Iran (Oman Sea)	Sea water	2.19-2.82	1.66-2.17	132.6-148.87	[19]
Iran	Oil produced water	7.92-68.12	B. G.- 30.73	B. G.- 65.34	This measurment

4. Conclusion

Natural radioactivity of Ra-226, Th-232 and K-40 were monitored in produced water from 10 desalinating complexes of Ahwaz, Maroon, Aghajari,Koranj, Rag sefid and Gachsaran oil fields. The measurments were performed using high resolution HPGe detection system. The lowest concentration of Ra-226 (7.92±0.74) was observed in Ahwaz 2 desalination complex and the highest concentration(68.12±0.087) was in Maroon 3 desalination complex. Concentration of Ra-226 in all samples was much higher than DRL (5 Bq/L) and EPA standard. Also the lowest concentration of Th-232 (background) was related to desalination complexes of rag sefid 1 and gachsaran , and its highest concentration (30.73±2.9) belonged to maroon 3 desalination complex. The highest K-40 specific radioactivity (34.65±1.36) was measured in ahwaz 1 desalination complex. The results of this reseach indicate high concentration Ra-226 in produced water. However, dose rate is in authorized area (18-93 nGy/h) and external hazard index is always less than unit.the TSS results varies from 48000 to 238000 mg/L, indicating high levels of sodium and chloride in

produced water. Therefore release of produced water in the environment causes soil erosion, soil contamination to chemicals and radioactive substances,pollution of ground water and surface water.

TABLE VI. EXTERNAL HAZARD INDEX FOR PRODUCED WATER SAMPLES

Sample name	*Place of sampling*	*D (nGy/h)*	*Effective Dose (μSv/yr)*	*External hazard index*
W1	Ahwaz 2 desalination plant	8.74	10.58	0.05
W2	Ahwaz 4 desalination plant	24.15	29.22	0.14
W3	Ahwaz 1 desalination plant	22.21	26.88	0.13
W4	Ahwaz 1 desalination plant	24.72	29.92	0.14
W5	Maroon 1 desalination plant	44.80	54.21	0.26
W6	Maroon 3 desalination plant	51.94	62.84	0.30
W7	Maroon 4 desalination plant	38.82	46.98	0.23
W8	Rag sefid 1 desalination plant	5.71	6.91	0.03
W9	Keranj Parsi desalination plant	9.47	11.47	0.05
W10	Gachsaran 2 desalination plant	5.91	7.16	0.03

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